

# Chemistry Fundamentals

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Almost all chemistry textbooks begin with a definition of chemistry, such as, **chemistry** is the study of **matter** and **energy** as well as their interactions. Further, common to textbooks are definitions such as matter is defined as anything that takes up space and has mass and energy is the ability to do **work**.

Textbooks usually continue with a section or two about the **scientific method** - a formal process for observing, recording data, and publishing explanations so that other scientists may repeat the experiment or process. It is the verifiability and repeatability of science that affords individuals to accept or reject explanations.

During the year long course, you should have been given an opportunity to complete several labs (experiments). At least one of these required labs will be on the AP exam free response or in the middle choice questions. In addition, you may be asked to identify the IV (**independent variable**) and the DV (**dependent variable**). The IV is a variable changed by the experimenter and the DV depends on the changes. Usually the results of the experiment are compared to a control.

Observations may be **qualitative** or **quantitative**; that is, using your senses or tools to record the quality of a substance compared to recording numbers during a quantitative activity.

Central to designing an experiment is the **hypothesis** - this is due to the nature of science using the **hypothetico-deductive** model. The experimenter initially provides a temporary explanation (called a hypothesis) that is tested by the variables.

After the observations, a summary of the data may result in a mathematical summary called a **law** or the experimenter may provide a representation of the data via a **model**. After numerous experiments, a **theory** may be developed and discussed. Competing theories may be available, allowing scientists to develop further experiments to test the theory.

# Measurement

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All measurements have two parts: the number and the units. The units give dimension to the quantity and are vital to understanding measurement. Without the units - nothing makes sense in chemistry. As I tell my students, numbers without units only work if you are trying to order a meal at McDonalds. In fact, the free response portion of the AP chemistry exam requires you to show that you have a firm grasp on units. Learn them. Today.

SI Units are the backbone to the AP Chemistry exam. In fact, many problems in chemistry can be solved by using ratios and following units. This means SI units should be memorized and unit conversions should be practiced.

Learning SI Units can be easily managed if you learn select base units, prefixes, and derived units. For example, length is measured in meters. Add the prefix milli (1/1000) and you have millimeters. As an additional example, units for volume are derived from other SI units. Length times width times height - or cubic meters - is the SI unit for volume. Chemists usually use liters ( $\text{dm}^3$ ) or milliliters ( $\text{cm}^3$ ).

## Length

Let's start with Length. Chemists might measure the distance between atoms in a chemical bond (bond length), we might measure the distance from the center of the atom (the nucleus) to the outermost electron (valence electron), we might also be interested in the length of a wave - or nanometers.

It is important to understand that length provides the first dimension for the size of atoms (the radius), taking us from a macroscopic view of materials to a microscopic view or atomic view.

Meters is the SI unit and we add prefixes to quickly get to the size of the atom. The smallest atom is the helium with a radius of 32 pm - a picometer is  $10^{-12}$  meters. The largest atom is cesium at 225 pm. You will want to be able to look at the periodic table and understand there are patterns for determining which atom is larger. The smallest are in the upper right hand corner and the largest are in the bottom left. Regardless, atoms are small - and no - your eye cannot see an atom without special tools.

For waves we add the prefix nano ( $10^{-9}$  meters). As a reference, visible light ranges in wavelength from 400 nm to 700 nm. You should learn this because chemists may use the qualitative flame test to identify metals in a salt and some calculations of wavelength may be involved in understanding energy given off by a blackbody (i.e., calculations using plank's constant).

## Mass

The next SI unit to master is mass, which is not the gravity induced concept of weight. Mass is simply the amount of matter and does not change, regardless of the material's position. Mass is the same on Earth or Pluto.

For mass, we tend to think of molar mass (the mass of one mole of a substance, usually grams per mole) or the mass of solute in a solvent (units of concentration). Additionally, important prefixes to learn for mass are kilo (1000) and milli (1/1000). For example, Enough solvent may be added to 32 mg of solute in order to make 400 mL of a solution. You will want to understand how to quickly and easily convert from one prefix to another.

Mass is measured with a balance, such as a triple-beam balance, electric balance, or as refined as an analytical balance. Your choice is based on the precision of the instrument required in the laboratory activity.

## Volume

The first derived unit to comprehend is volume. Density is the second important derived unit for chemistry students to learn.

Volume is the space a substance occupies and is derived from length, multiplying length times width times height, or cubic meters. Chemists typically discuss volume using the units liters or milliliters.

We measure volume with a graduated cylinder - or chemical droppers for small amounts - pipets for tiny amounts - or we might measure volume through volumetric pipets (also called burettes) in titration. Micropipetts are commonly used in biochemistry labs.

## Density

The second derived unit chemistry learners should master is density. Among other topics, density is used in gas calculations. Density is mass per unit volume. Chemists tend to use grams per milliliter (g/mL) or grams per cubic centimeter (g/cm<sup>3</sup>).

Archimedes used density to expose a fraudulent King's crown. Because the shape of the crown is asymmetrical, he measured volume by placing the crown in water. After measuring the mass, he calculated the density and showed that the density of the crown did not match that of gold.

Calculate the mass of 40.0 mL of methanol, given the density of methanol is 0.790 g/mL.

Rearrange the equation density = mass / volume

mass = volume x density

mass = 40 mL x 0.790 g/mL

mass = 31.6 g

### Temperature

The measure of the average kinetic energy is temperature and is measured with a thermometer. Gas problems require students to convert degrees Celsius to kelvins. Increments for each scale are exactly the same, thus if a problem provides degrees Celsius then simply add 273.15.

$$K = ^\circ C + 273.15$$

Remember: The Kelvin temperature scale is absolute. Based on the Kinetic Molecular Theory, no molecular motion occurs at zero kelvin ( $-273.15^\circ C$ ). No negative kelvins exist.

### Pressure

The amount of force per area is pressure and is measured with a barometer. The SI Unit is Pascal but the common units are mmHg or atm.

#### Units of Pressure

Unit	Symbol	Definition / Relationship
Pascal	Pa	Si Unit $1 \text{ Pa} = 1 \text{ N} / \text{m}^3$
Millimeter of mercury	Mm Hg	
Atmosphere	atm	Average atmospheric pressure at sea level and $0^\circ C$
Torr	torr	$1 \text{ torr} = 1 \text{ mm Hg}$

Equivalency statement

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101.3 \text{ kPa}$$

Gas molecules exert force, and therefore pressure, on any surface with which they collide. Gas law problems require you to focus on the units - so the easiest is to convert to atm units and stick with an "easy" universal gas constant.

### Prefixes

kilo  $1 \text{ kg} = 1000 \text{ g}$

centi-  $100 \text{ cg} = 1 \text{ g}$

milli-  $1000 \text{ mg} = 1 \text{ g}$

micro  $10^6 \text{ ug} = 1 \text{ g}$

nano-  $10^9 \text{ ng} = 1 \text{ g}$

## Uncertainty in measurement

Every measurement has uncertainty associated with it. The **uncertainty** depends on the precision of the measurement. **Precision** is the repeatability of the measurement. During a lab we repeat the measurement several times, called trials, and average the results. Recall the repeatability is a fundamental concept of any science.

For example, do the following substances have the same mass?

Substance	Over-the-counter scale	Analytical balance
#1	2.4 g	2.385 g
#2	2.4 g	2.443 g

The answer to this question depends on the instrument because the precision of the instrument influences the conclusion.

Note. Uncertainty is identified in the significant figures shown; that is, the amount of numbers recorded. The greater number of significant figures leads to lower degree of uncertainty.

# Atomic Theory

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The science of chemistry and philosophy overlap, with roots in the Ancient Greek society. The Stanford encyclopedia summarizes the history of chemistry with the premise that **Aristotle** was the founder of chemistry because of his publications that systematically recorded observations about nature. Aristotle's basic thesis extended work by **Empedocles**; that is, elements are Earth, Fire, Water, and Air. Most important, Aristotle attempted to explain the observations regarding different physical properties of substances.

The theory proposed by Empedocles was challenged by **atomism**, the idea that the world is composed of atoms and void. Atoms were defined as 'uncuttable' - a-tomos or not cuttable. However, the challenge did not become the dominate theory for almost 2,000 years later.

## Dalton

John Dalton (1766 - 1844) was an English schoolteacher interested in physics and meteorology. From 1787 until his death, he kept daily weather records. From these records Dalton developed his theory of the atom.

Dalton calculated atomic weights from percent compositions of compounds. He concluded chemical elements are specific types of atoms and these atoms combine in integral ratios. Dalton's postulates were:

1. All matter is composed of tiny particles called atoms.
2. Atoms of like elements are identical, while elements of different elements are different
3. Atoms are indestructible and unchangeable; they are neither created nor destroyed in chemical reactions, nor do they change forms
4. Compounds are formed when atoms of different elements combine in whole-number ratios

These postulates led Dalton to develop his model - atoms are tiny, indivisible, indestructible particles.

## Thomson (Plum Pudding)

The late 1800s and early 1900s can be characterized as a time of incremental changes to the atomic theory. Both physicists and chemists spent time and energy developing experiments to understand the atom.

In 1891, **George Stoney** suggested the fundamental unit of electricity is an electron. While the idea of an electron existed for several decades after John Dalton's publications discussions centered around particular nature of matter and using wave concepts to explain

observations of matter. Additionally, the invention of a Crooke's tube led some experimentalists to the idea that the rays coming out of these tubes were waves.

In 1897, **J. J. Thomson** published his work in which he designed an experiment that provided evidence that a subatomic particle exists. Thomson not only identified the electron, he also identified the charge and the charge-to-mass ratio.

Using a **cathode ray tube** (streams of 'rays'), magnets, and electrically charged plates - Thomson showed the 'rays' deflect as the magnet comes close to the stream. He interpreted the results to mean smaller particles - which he called corpuscles - were inside the atom.

In 1909, **Robert Millikan** published his famous oil-drop experiment used to determine the mass of the electron.

For several years, Thomson explained the results of his experiments using a "Plum Pudding" model; that is, a positive sphere contains embedded negatively charged electrons spread evenly throughout the sphere.

### **Rutherford (Nuclear Atom)**

Ernest Rutherford and his students carried out the most ingenious series of experiments to understand the atom. Using radioactive material, the malleable property of metals, and material the "lights up" when hit with radioactive particles, Rutherford was able to test Thomson's model of the atom.

**Alpha particles** (helium nuclei) were fired into a thin layer of gold. The majority of these particles passed through the metal, however, some were deflected.

Rutherford explained these results with the development of a nuclear atom. The nucleus contained the positive portion of the atom, and the electrons carried a negative charge.

Years later, Rutherford's student, **James Chadwick**, identified another nuclear subatomic particle called neutrons.

### **Bohr (Planetary Model)**

Max Planck, Albert Einstein, and Niels Bohr studied blackbody emission. Their work is known as the precursor to quantum mechanics.

Planck noted the energy absorbed or emitted from atomic spectra of glowing bodies (blackbody emission) was in fixed amounts, called **quanta**. Mathematically, he proposed the following equation:

$E = h\nu$ , where E is the energy, h is known the constant known as Planck's constant,  $\nu$  is the frequency of the wave.

In 1905, Albert Einstein proposed the photoelectric effect. Light of particular frequency hit metal and emits electrons from the substance. He concluded light is composed of tiny packets of energy called **photons**. This conclusion led to a wave-particle duality of light.

Bohr developed a new model of the atom, in which electrons were in fixed orbits rather than scattered throughout the atom. Working with hydrogen spectra, Bohr suggested the spectra developed from electrons moving from an excited state to a ground state.

The Bohr model explained the hydrogen spectrum very well but it failed to explain the spectra of all other atoms.

Loius de Broglie proposed matter should have wave-like properties. Additional spectra analysis of elements supported a new model of the atom, called the wave model.

In this model, orbits do not exist. Instead, orbitals that match spectra are discussed. These orbitals are *s* (sharp), *p* (principal), *d* (diffuse), and *f* (fundamental). Orbitals do not describe the path or motion of the electron. Instead, they describe the probability of finding an electron at a particular time.

Wave theory is discussed in greater detail in a different chapter so that emphasis can be placed on electron configurations.

The most modern atomic model is not tested in the AP Chemistry exam; that is, the standard model.

# Atomic Structure

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Protons = identity of atom  
Neutrons = stability of atom, isotopes  
Electrons - chemical behavior of atom

In the previous chapter, you were introduced to the different models of the atom. While the standard model is the latest, chemists focus on the three subatomic particles: protons, neutrons, and electrons.

## Summary Table

	Place	Charge	Relative mass	Actual mass
e <sup>-</sup>	Cloud	-	1/1837	9.11 x 10 <sup>-28</sup>
p <sup>+</sup>	nucleus	+	1	1.67 x 10 <sup>-24</sup>
n <sup>0</sup>	nucleus	0	1	1.68 x 10 <sup>-24</sup>

## Atomic Number (Z)

1. The number of protons in the nucleus of each atom of that element
2. Atoms are identified by their atomic number
3. Because atoms are neutral,
4. # protons = # electrons
5. Periodic Table is in order of increasing atomic number

## Mass Number (A)

1. The total number of protons and neutrons in the nucleus of an isotope

## Percent Abundance Problem

Iron-54	5.90%	53.94
Iron-56	91.72%	55.93
Iron-57	2.10%	56.94
Iron-58	0.28%	57.93

Average atomic mass = (0.0590 \* 53.94) + (0.9172 \* 55.93) + (0.0210 \* 56.94) + (0.0028 \* 57.93) = 55.8394 amu

### Sample Problem

The atomic mass of an element is 69.72. Two isotopes exist, E-70 and E-69. What is the natural abundance of each isotope?

$$70x + 69(1 - x) = 69.72$$

$$70x + 69 - 69x = 69.72$$

$$-1x = 0.72$$

Therefore, E-69 = 28% and E-70 = 72%

### Electrons

1. The volume of an atom is from the area in which the electrons move
2. The chemical properties of an atom arise from the electrons.

Calculating the number of electrons, protons, and neutrons.

A = protons + neutrons

Z = protons

Therefore, to get the number of neutrons, subtract A - Z

### Isotopes

1. Atoms of the same element that have different masses
2. All elements of the same element have the same number of protons but may vary in the number of neutrons
3. All isotopes have different masses
4. Similar chemical behavior

### Designating isotopes

There are two ways to record isotopes: hyphen notation and nuclear symbols.

#### *Hyphen notation*

The mass number (A) is written after the name of the element. For example, hydrogen-2, also called deuterium.

#### *Nuclear symbol*

The letters X, A, Z, and C



Mass number = 2    Atomic number = 1



Mass number = 4    Atomic number = 2

### Ion formation

Ions are formed by the loss or gain of an electron.

Metals tend to lose electrons, leading to a positive ion called a **cation**.



Nonmetals tend to gain electrons, leading to a negative ion called an **anion**.



### Memorize the following:

Group 1 tend to lose 1 electron

Group 2 tends to lose 2 electrons

Group 3 (except boron) tend to lose 3 electrons

Group 16 (Group 6A) tend to gain 2 electrons

Group 17 (Group 7A) tend to gain 1 electron

Transition metals form cations with various charges

# Wave Model

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## Quantum numbers

1. Principal Quantum Number ( $n$ ),  
1, 2, 3, 4...
2. Angular Momentum Number ( $l$ ),  
0, 1, 2 ... up to  $n-1$
3. Magnetic Quantum Number ( $m_l$ ),  
between  $-l$  and  $+l$
4. Spin Quantum Number ( $m_s$ ),  
 $+\frac{1}{2}$ ,  $-\frac{1}{2}$

## Electron configurations

1. s, p, d, and f
2. Aufbau, Hund's rule, Heisenberg's uncertainty principle

## Quantum Numbers

### Principal Quantum Number ( $n$ )

Determines the energy level of the atom  
Starts at 1 and increases to infinity

$n=1$ ,  $n=2$ ,  $n=3$ ,  $n=4$

### Angular Momentum Number ( $l$ )

The  $l$  corresponds to the subshell

0, 1, 2 ... up to  $n-1$

### Magnetic Quantum Number ( $m_l$ )

Assignment of the electron to a particular orbital

between  $-l$  and  $+l$

### Spin Quantum Number ( $m_s$ )

The spin of the electron

$+1/2, -1/2$

## Sample AP Question

Which set of quantum numbers are incorrect?

- A. 4, 1, 0, 1/2
- B. 4, 2, 1, 1/2
- C. 4, 3, 2, 1/2
- D. 4, 4, 3, 1/2

In choice D, the angular momentum number is 4, an impossible number because the  $l$  number cannot be greater than  $n-1$ .

### Electron Configurations

A method for showing the location of electrons in energy levels and sublevels. The superscript is the number of electrons. The video will walk you through how to write electron configurations. Keep in the mind the following ideas or rules:

**Valence electrons:** the electrons in the outermost (highest) principal energy level of an atom.

**Core electrons:** inner electrons, which are not involved in bonding atoms to each other.

**Aufbau Principle:** An electron occupies the lowest-energy orbital that can receive it

**Pauli Exclusion Principle:** No two electrons in the same atom can have the same set of four quantum numbers

**Hund's Rule:** Orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin

### Orbital Notation

1. Unoccupied orbitals are represented by a line, \_\_\_\_\_
  - a. Lines are labeled with the principal quantum number and the sublevel letter
2. Arrows are used to represent electrons
  - a. Arrows pointing up and down indicate opposite spins

### Configuration Notation

1. The number of electrons in a sublevel is indicated by adding a superscript to the sublevel designation

Hydrogen =  $1s^1$

Helium =  $1s^2$

Lithium =  $1s^2 2s^1$

### Exceptional Electron Configurations

#### 1. Irregularity of Chromium

a. Expected:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

b. Actual:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

#### 2. Irregularity of Copper

a. Expected:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

b. Actual:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

3. Numerous transition and rare-earth elements transfer electrons from smaller sublevels in order to half-fill, or fill, larger sublevels.

# Periodic Table

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## The Periodic Law

The physical and chemical properties of the elements are periodic functions of their atomic numbers.

Elements on the table are arranged in order of increasing atomic number (number of protons)

### A. Metals

1. Good conductors of heat and electricity
2. Lustrous (shiny)
3. Solids (except mercury)
4. Ductile (can be drawn into wire)
5. Malleable (can be hammered into thin sheets)

### B. Nonmetals

1. Poor conductors of heat and electricity
2. Most are gaseous
3. Solids tend to be brittle

### C. Metalloids

1. Some properties of metals, some of nonmetals

## Periods and the Blocks of the Periodic Table

### A. Periods

1. Horizontal rows on the periodic table
2. Period number corresponds to the highest **principal quantum number** of the elements in the period

### B. Sublevel Blocks

1. Periodic table can be broken into blocks corresponding to *s, p, d, f* sublevels

## Blocks and Groups

### A. s-Block, Groups 1 and 2

1. Group 1 - **The alkali metals**
  - a. One s electron in outer shell
  - b. Soft, silvery metals of low density and low melting points
  - c. Highly reactive, never found pure in nature

2. Group 2 - **The alkaline earth metals**
  - a. Two s electrons in outer shell
  - b. Denser, harder, stronger, less reactive than Group 1
  - c. Too reactive to be found pure in nature
- B. d-Block, Groups 3 - 12
  1. Metals with typical metallic properties
  2. Referred to as "**transition**" metals
  3. Group number = sum of outermost s and d electrons
- C. p-Block elements, Groups 13 - 18
  1. Properties vary greatly
    - a. **Metals**
      - (1) Softer and less dense than d-block metals
      - (2) Harder and more dense than s-block metals
    - b. **Metalloids**
      - (1) Brittle solids with some metallic and some nonmetallic properties
      - (2) Semiconductors
    - c. **Nonmetals**
      - (1) **Halogens** (Group 17) are most reactive of the nonmetals
- D. f-Block, Lanthanides and Actinides
  1. **Lanthanides** are shiny metals similar in reactivity to the Group 2 metals
  2. **Actinides**
    - a. All are radioactive
    - b. Plutonium (94) through Lawrencium (103) are man-made.

# Periodicity

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Periodic relationships include: atomic radii, electronegativity, ionization energies, and electron affinities.

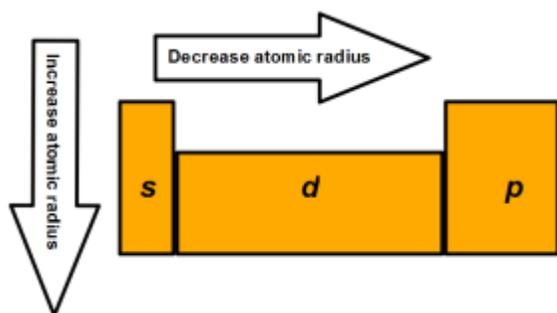
By organizing the elements by atomic number, patterns of physical and chemical properties are seen.

## Atomic radius

One half the distance between nuclei of identical atoms chemical bound.

Atomic radius decreases across a period due to an increase in an effective positive nuclear charge.

Atomic radius increases down a group due to increasing number of energy levels such that the outer electrons are farther from the nucleus.

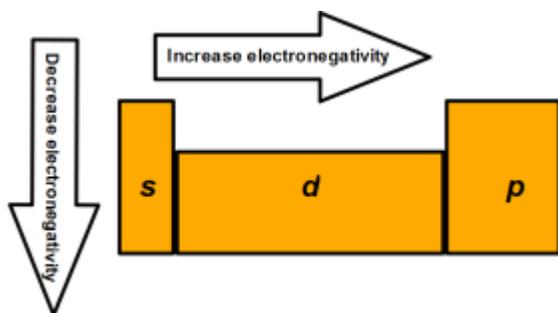


## Electronegativity

The attraction for electrons from a bonded atom.

Electronegativity increases across a period due to greater attraction of the electrons, "attempt of atom to get to noble gas configuration".

Electronegativity decreases down a period.



### Ionization energy

Ionization is any process resulting in the formation of an ion. Ionization energy is the energy required to remove one electron from a neutral atom of an element, measured in kilojoules/mole (kJ/mol).

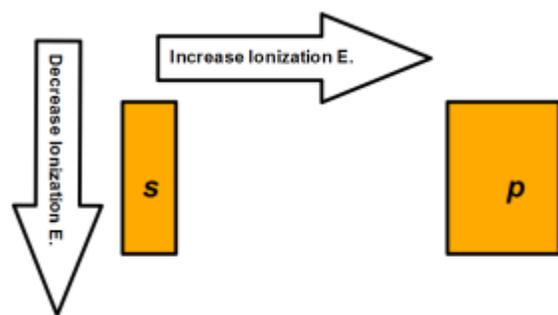
Ionization energy of main-group elements tends to increase across each period because atoms are getting smaller and electrons are closer to the nucleus.

Ionization energy of main-group elements tends to decrease as atomic number increases in a group because atoms are getting larger; electrons are farther from the nucleus thereby outer electrons are more shielded by inner electrons.

Metals have characteristic low ionization energy.

Nonmetals have high ionization energy.

Noble gases have very high ionization energy.



### Sample AP Question

To which group does element E most likely belong?

Ionization energy for Element E (kJ/mol)

First	Second	Third	Fourth	Fifth
520	1450	2630	12931	18459

- A. Alkali metals
- B. Alkaline earth metals
- C. Boron family
- D. Carbon family
- E. Nitrogen family

The answer is the boron family because of the large increase that happens between the third and fourth ionization energies.

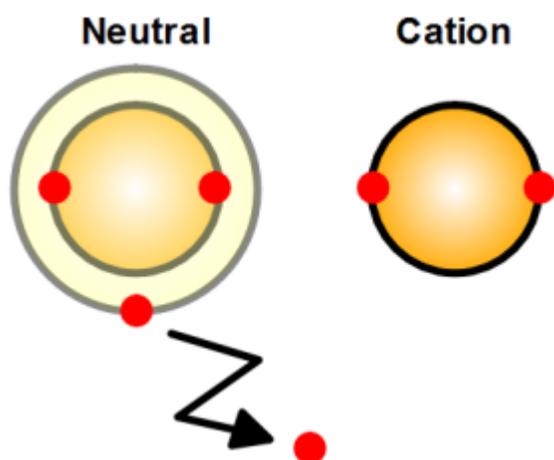
### Removing additional electrons.

Ionization energy increases for each successive electron because each electron removed experiences a stronger effective nuclear charge.

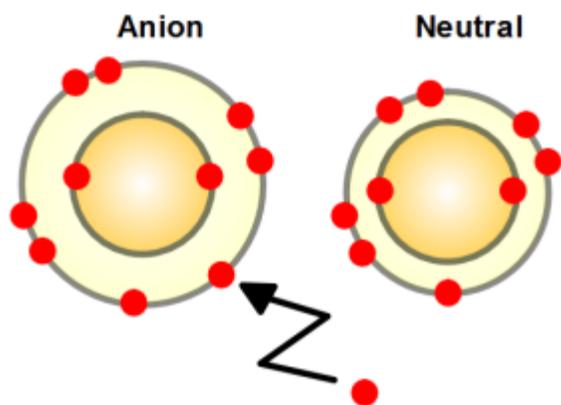
The greatest increase in ionization energy comes when trying to remove an electron from a stable, noble gas configuration.

### Trends in ion size

Cations are smaller than the corresponding neutral atom because protons outnumber electrons and there is less shielding.



Anions are larger than the corresponding neutral atom because electrons outnumber protons and there is greater electron-electron repulsion.

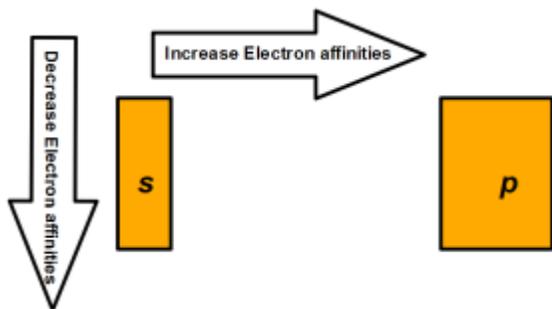


## Electron affinities

The energy given off when a neutral atom in the gas phase gains an extra electron to form a negatively charged ion.

Increases across a period due electron repulsions.

Decreases down a group because the new electron is being placed in a larger orbital (farther from the nucleus).



# Nomenclature

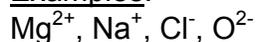
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Memorization is the best method for this information. Use the flashcards to practice the names of polyatomics and the common ions.

## Monatomic Ions

Ions formed from a single atom

Examples:



Representative elements: elements in *s* and *p* block, except the noble gases.

## Monatomic cations:

a. Identified by the element's name

Examples:

$\text{Mg}^{2+}$  = magnesium ion

$\text{Na}^+$  = sodium ion

## Monatomic anions:

a. Drop the ending of the element name

b. Add an -ide ending

Examples:

$\text{F}^-$  = Fluoride

$\text{Cl}^-$  = Chloride

## Naming and Writing formulas for ionic compounds

### Binary Compounds

Compounds composed of two different elements

## Naming Binary Ionic Compounds from their formula

1. Name the cation
2. Name the anion

### Examples:

$\text{MgCl}_2$  = magnesium chloride

$\text{MgO}$  = magnesium oxide

$\text{K}_2\text{O}$  = potassium oxide

## The Stock System of Nomenclature

Metals in the transition block may give off different number of electrons. For example, lead might release 2 or 4 electrons. Alfred Stock developed a method to identify the number of electrons lost.

1. Roman numerals are used to denote the charge of metals that can form two or more cations
2. The numeral is enclosed in parenthesis and placed immediately after the metal name a. Iron (II) and Iron (III), pronounced "Iron two" and "Iron three"
3. Roman numerals are never used:
  - a. For anions
  - b. For metals that only form one ion

### Examples:

$\text{CuO}$  = copper(II) oxide

$\text{Cu}_2\text{O}$  = copper(I) oxide

## Writing Formulas for Binary Ionic Compounds

1. Write the symbol for the ions side by side. ALWAYS write the cation FIRST!!!
2. Cross over the charges by using the absolute value of each ion's charge as the subscript for the other ion
3. Check that the subscripts are in smallest whole number ratio

### Example:

Write the formula for aluminum oxide.



The three becomes the subscript for the oxide and the two becomes the subscript for the aluminum.



## Naming compounds containing polyatomic

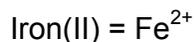
1. Same as for monatomic ions

## Writing formulas including polyatomic ions

1. Use parenthesis when you need MORE THAN ONE of a polyatomic ion.
2. Parentheses are NEVER used for monatomic ions, regardless of how many are in the formula.

### Example:

Iron(II) phosphate



Crisscross method



# Chemical Bonding

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## **Intramolecular Forces**

Chemical bonds are electrostatic interactions (an electromagnetic force) between valence electrons; a bond is a force that holds groups of two or more atoms together and makes them function as a unit. The strength of these bonds is measured by the energy it takes to break the bonds and this is called bond energy.

## **Electrostatic charges**

Charge is the fundamental property of forms of matter that exhibit electrostatic attraction or repulsion in the presence of other matter. Electric charge is a characteristic property of many subatomic particles. The charges of free-standing particles are integer multiples of the elementary charge  $e$ ; we say that electric charge is quantized. Michael Faraday, in his electrolysis experiments, was the first to note the discrete nature of electric charge. Robert Millikan's oil-drop experiment demonstrated this fact directly, and measured the elementary charge.

By convention, the charge of an electron is  $-1$ , while that of a proton is  $+1$ . Charged particles whose charges have the same sign repel one another, and particles whose charges have different signs attract.

Coulomb's law quantifies the electrostatic force between two particles by asserting that the force is proportional to the product of their charges, and inversely proportional to the square of the distance between them.

Atoms typically have equal numbers of protons and electrons, in which case their charges cancel out, yielding a net charge of zero, thus making the atom neutral.

## **Electronegativity**

When different atoms interact, a bond can form in which electrons are shared – either equally or unequally. How electrons are shared can be described by a property called electronegativity: the relative ability of an atom to attract one or more electrons to it.

1. When the atoms in a molecule are the same, the bonding electrons are shared equally, and the bond is a nonpolar covalent bond.
2. When two different atoms are joined by a covalent bond and the bonding electrons are shared unequally, the bond is called a polar covalent bond. The atom with the stronger electron attraction (the more electronegative atom) in a polar bond acquires a slightly negative charge. The less electronegative atom acquires a slightly positive charge.

This chapter focuses on the idea of ionic compounds and molecular compounds. These compounds involve ionic bonds (those between ions with opposite charges) and covalent bonds (electrons shared between atoms in molecules).

Ionic bond: Chemical bonding by transferring electrons

Metals and non-metals react to form cations (metals) and anions (non-metals). These compounds are held together by the charges on the ions involved – ionic bonds.

Covalent bond: Chemical bonding by electron sharing by nuclei

Many compounds are not made of ions. The nonionic compounds consist of atoms bonded tightly together in the form of molecules. The bonds form when pairs of electrons are shared between atoms. Such bonds are called covalent bonds. Electron pairs are shared, and a covalent bond forms between two atoms when both atoms are nonmetals (also hydrogen).

a. **Nature of the Covalent Bond**

A covalent bond consists of a pair of electrons of opposite spin filling an atomic orbital on both of the bonded atoms. At any instant the two electrons being shared may be located at any of various points around the two nuclei. There is, however, a greater probability of finding the two electrons.

**Electron Dot Notation**

- a. An electron-configuration notation in which only the valence electrons of an atom of a particular element are shown, indicated by dots placed around the element's symbol
- b. Inner (core) electrons are not shown

**Intermolecular Forces**

Forces acting between substances are called intermolecular forces. These forces are different from the intramolecular forces (chemical bonds) that hold a molecule together. Sometimes these forces are referred to as van der Waals forces.

These forces are responsible for determining whether a compound is a gas, a liquid, or a solid at a given temperature.

1. Water is a polar molecule (there is a dipole moment). Molecules with dipole moments align so that positive and negative ends are close to each other. This alignment is called a dipole-dipole attraction.
  - Electrostatic attractions between opposite charged regions
  - These forces become weak as distance increases.
  - Dashes are used to describe these forces

1. Hydrogen Bonding

- A special type of dipole-dipole attraction is called hydrogen bonding. Hydrogen covalently bound to nitrogen, oxygen, or fluorine (high electronegativity elements).
  - Strongest of the dipole-dipole interactions
  - Important in water and biomolecules (proteins, DNA)
1. London Dispersion Forces
    - Forces between noble gas atoms and nonpolar molecules are called London dispersion forces.
    - Caused by the motion of electrons
    - Transitory force (not permanent)
    - Weaker than dipole-dipole attractions

## Lewis Structures

### A. Unshared Pairs (Lone Pairs)

1. A pair of electrons that is not involved in bonding and that belongs exclusively to one atom

### B. Lewis Structures

1. Formulas in which atomic symbols represent nuclei and inner-shell electrons, dot pairs or dashes between two atomic symbols represent electron pairs in covalent bonds, and dots adjacent to only one atomic symbol represent unshared electrons

### C. Structural Formula

1. Formulas indicating the kind, number, arrangement, and bonds but not unshared pairs of the atoms in a molecule

### D. Drawing Lewis Structures (trichloromethane, $\text{CHCl}_3$ as an example)

1. Determine the type and number of atoms in the molecule  
1 x C, 1 x H, 3 x Cl
2. Write the electron dot notation for each type of atom in the molecule
3. Determine the total number of valence electrons to be combined

Element	Number of Atoms	Number of e-	Total
H	1	1	1
Cl	3	7	21
C	1	4	4
Total			26 e-

4. Arrange the atoms to form a skeleton structure for the molecule. If carbon is present, it is the central atom. Otherwise, the least electronegative element atom is central (except for hydrogen, which is never central). Then connect the atoms by electron-pair bonds

5. Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons

6. Count the electrons in the structure to be sure that the number of valence electrons used equals the number available

Note: These six steps can be condensed into three steps

1. Count valence electrons
2. Place bonding electrons
3. Place non-bonding electrons

Please view the video on drawing Lewis structures.

### Geometry of molecules

**There is only one way to handle this topic - memorize.**

VSEPR = Valence Shell Electron Pair Repulsion

The electrons repel each other.

Predicts the shapes of a covalent molecule and polyatomic ions

Geometry	Lone e- pairs	Formula	Example	Bond angle
Linear	0	AX2	CO <sub>2</sub>	180
Trigonal Planar	0	AX3	BF <sub>3</sub>	120
Tetrahedral	0	AX4	CH <sub>4</sub>	109.5
Trigonal-bipyramidal	0	AX5	PF <sub>5</sub>	90 / 120
Octahedral	0	AX6	SF <sub>6</sub>	90
Bent	1	AX2E	SeO <sub>2</sub>	
Trigonal Pyramidal	1	AX3E	NH <sub>3</sub>	
SeeSaw	1	AX4E	SF <sub>4</sub>	
Square-Pyramidal	1	AX5E	BrF <sub>5</sub>	
Bent	2	AX2E2	H <sub>2</sub> O	

T-shape	2	AX3E2	ICl <sub>3</sub>	
Square Planar	2	AX4E2	XeF <sub>4</sub>	
Linear	3	AX2E3	XeF <sub>2</sub>	

## Valence Bond Theory

Orbitals overlap to form bonds

Sigma Bond (All Single Bonds)

Overlap of 2 s orbitals (H-H)

Overlap of an s and a p orbital (H-Cl)

Overlap of 2 p orbitals (Cl-Cl)

Pi Bond

Overlap of 2 p orbitals (C=C)

Double bonds have 1 sigma and 1 pi bond

Triple bonds have 1 sigma and 2 pi bonds

## Hybridization

Geometry	Electron pairs	Hybridization
Linear	2	sp
Trigonal Planar	3	sp <sup>2</sup>
Tetrahedral	4	sp <sup>3</sup>
Trigonal bipyramidal	5	sp <sup>3</sup> d
Octahedral	6	sp <sup>3</sup> d <sup>2</sup>

## Sample AP Problem

Contains 1 sigma and 2 pi bonds

1. Br<sub>2</sub>
2. N<sub>2</sub>
3. O<sub>2</sub>
4. F<sub>2</sub>

The diatomic nitrogen gas contains a triple bond. Diatomic oxygen has a double bond. Fluorine and Bromine have single bonds.

# Gases

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Laws of ideal gases  
Equation of state for an ideal gas  
Partial pressures  
Kinetic molecular theory  
Interpretation of ideal gas laws on the basis of this theory  
Avogadro's hypothesis and the mole concept  
Dependence of kinetic energy of molecules on temperature  
Deviations from ideal gas law

## Properties of Gases

### 1. Expansion

Gases do not have a definite shape or volume

Gases take the shape of their containers

Gases evenly distribute themselves within a container

### 2. Fluidity

Gas particles easily flow past one another

### 3. Low Density

A substance in the gaseous state has 1/1000 the density of the same substance in the liquid or solid state

### 4. Compressibility

Gases can be compressed, decreasing the distance between particles, and decreasing the volume occupied by the gas

## The Kinetic Theory and a Model for Gases

### Assumptions of the Kinetic-Molecular Theory

1. Gases consist of large numbers of tiny particles that are far apart relative to their size
2. Gas particles undergo elastic collisions; that is, collisions in which no energy is lost
3. Gas particles are in constant, rapid motion. They therefore possess kinetic energy, the energy of motion

## Kinetic Energy and Temperature

Formula for Kinetic Energy

$KE = \frac{1}{2} mv^2$ , where  $m$  = mass and  $v$  = speed

### Relationship to Temperature

1. The average kinetic energy of gas particles depends on the temperature
2. All gases at the same temperature have the same average kinetic energy
  - a. Small molecules (small mass,  $m$ ) have higher average speeds
3. Kelvin temperature is directly proportional to the average kinetic energy of a substance

0 Kelvin = absolute zero = NO kinetic energy

### Boyle's Law

1. The volume of a fixed mass of gas varies inversely with the pressure at constant temperature
  - a. Volume  $\uparrow$  as pressure  $\downarrow$
  - b. Volume  $\downarrow$  as pressure  $\uparrow$
2. Mathematical Statement of Boyle's Law
  - a. For identical masses of gas, at constant temperature  
 $P_1V_1 = P_2V_2$

### Charles's Law

1. The volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature

Charles's Law Mathematically

1. For identical masses of gases, at constant pressure:  
 $V_1/T_1 = V_2/T_2$

### Gay-Lussac's Law

1. The pressure of a fixed mass of gas at constant volume varies directly with the Kelvin temperature
2. For identical masses of gases, at constant volume:

### The Combined Law

A mathematical expression of the relationship between pressure, volume and temperature of a fixed amount of gas (constant mass) (in real life experiments, pressure, volume and temperature may all change)

### **Ideal Gas Law**

The mathematical relationship of pressure, volume, temperature, and the number of moles of a gas.

1. Mathematically:  $PV = nRT$ 
  - a.  $P$  = Pressure in atmospheres
  - b.  $V$  = Volume in liters
  - c.  $n$  = # of moles
  - d.  $T$  = Temperature in Kelvins
2. The ideal gas law reduces to Boyle's, Charles's, or Gay-Lussac's Law if the necessary variable is held constant

### **The Ideal Gas Constant**

1. Units for  $R$  depend on units of measurement used for  $P$ ,  $V$ , and  $T$
2. For units of kilopascals, liters, and Kelvins
3. For units of atmospheres, liters, and Kelvins:

Finding  $P$ ,  $V$ ,  $T$  or  $n$

1. Three of the four variables must be known in order to use the ideal gas law

### **Finding Molar Mass Using the Ideal Gas Law**

#### **Sample AP Problem**

The density of an unknown gas at STP is 0.870 g/L. Find the molar mass.

Rearrange the ideal gas law:

$$PV = nRT$$

$$n = \text{mass} / \text{molar mass}$$

$$PV = (\text{mass})RT / \text{molar mass}$$

$$\text{molar mass}(P) = (\text{mass})RT / V$$

$$\text{density} = \text{mass} / V$$

Therefore,

$$\text{molar mass (P)} = d * RT$$

$$d = \text{molar mass (P)} / RT$$

Or easier to show

$$d = PM / RT$$

M = molar mass (g/mol)

R = 0.0821 L-atm/K-mol

Therefore

$$0.870 \text{ g/L} = 1 \text{ atm (M)} / R (273\text{K})$$

$$M = 19.5 \text{ g/mol}$$

### **Ideal Gas versus Real Gas**

Ideal Gas

1. An imaginary gas that perfectly fits all the assumptions of the kinetic-molecular theory

Real Gases

1. A gas that does not behave completely according to the assumptions of the kinetic-molecular theory.
2. Real gases occupy space and exert attractive forces on one another

Likely to behave nearly ideally	Likely not to behave ideally
Gases at high temperature and low pressure	Gases at low temperature and high pressure
Small non-polar gas molecules	Large, polar gas molecules

### **Partial Pressure**

1. The pressure exerted by each gas in a mixture

### **Dalton's Law**

1. The total pressure of a mixture of gases is equal to the sum of the partial pressures of the component gases

# Liquids and Solids

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1. Liquids and solids from the kinetic-molecular viewpoint
2. Phase diagrams of one-component systems
3. Changes of state, including critical points and triple points
4. Structure of solids; lattice energies

## Properties of Liquids

### Surface Tension

Force of attraction between molecules in liquids

### Cohesion

Controls the shape of the liquid

### Adhesion

Force between liquid and the container

### Viscosity

The resistance of a liquid to flow

### Vapor pressure

Pressure of the vapor present at equilibrium

### Boiling point

Boiling point is when the vapor pressure equals atmospheric pressure

## Phase Changes

### Vaporization (Evaporation)

The escape of molecules from the surface to form a gas

Vaporization is always endothermic

Heat of vaporization (Enthalpy of vaporization) is the energy required to vaporize one mole of liquid at 1 atm.

### Vapor Pressure

Pressure of the vapor present at equilibrium

## **Boiling and Condensation**

### **Boiling**

The conversion of a liquid to a vapor within the liquid as well as at its surface. It occurs when the equilibrium vapor pressure of the liquid equals the atmospheric pressure

### **Boiling Point**

The temperature at which the equilibrium vapor pressure of the liquid equals the atmospheric pressure

- a. Water boils at 100 °C at 1 atm pressure
- b. Water boils above 100 °C at higher pressures
- c. Water boils below 100 °C at lower pressures

### **Condensation**

The conversion of a gas to a liquid by the removal of energy

## **Freezing and Melting**

### **Freezing Point**

The temperature at which the solid and liquid are in equilibrium at 1 atm

For pure crystalline solids, the melting point and freezing point are the same

Temperature remains constant during a phase change

## **Sublimation and Deposition**

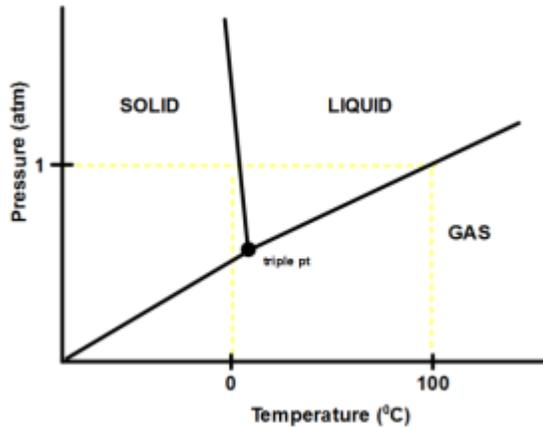
Sublimation is the change of state from a solid directly to a gas

1. Dry ice is gaseous CO<sub>2</sub>
2. Reasons for sublimation
  - a. Solids have very low vapor pressure

Deposition is the change of state from a gas directly to a solid

## Phase Diagrams

A graph of pressure versus temperature that shows the conditions under which the phases of a substance exist (notice that pressure is on a logarithmic scale)



### Triple Point

All three phases exist together in equilibrium

The temperature and pressure conditions at which the solid, liquid, and vapor of the substance can coexist at equilibrium

### Critical Temperature

The temperature at above which the substance cannot exist in the liquid state, regardless of pressure

For water, the critical temperature is  $373.99^{\circ}\text{C}$

### Critical Pressure

The lowest pressure at which the substance can exist as a liquid at the critical temperature

For water, the critical pressure is 217.75 atm

### Critical Point

The point on the graph describing simultaneously the critical temperature and the critical pressure

$P = 217.75 \text{ atm}$

Temperature =  $373.99 \text{ }^{\circ}\text{C}$

For pure crystalline solids, the melting point and freezing point are the same

Temperature remains constant during a phase change

### **Sublimation and Deposition**

Sublimation is the change of state from a solid directly to a gas

Dry ice > Gaseous CO<sub>2</sub>

Deposition is the change of state from a gas directly to a solid

### **Energy of Phase Changes**

#### **Freezing and Melting**

##### **Molar Heat of Fusion**

The amount of heat energy required to melt one mole of solid at its melting point

##### **Molar Heat of Solidification**

The amount of heat energy released when one mole of a liquid freezes to a solid at its freezing point

#### **Vaporization and Condensation**

##### **Molar Heat of Vaporization**

The amount of heat energy required to vaporize one mole of a liquid at its boiling point

##### **Molar Heat of Condensation**

The amount of heat energy released when one mole of a vapor condenses to a liquid at its condensation point

Strong attractive forces between particles result in high molar heat of vaporization/condensation for water

##### **Heat of Solution**

Heat released or absorbed as a solute associates with the solvent during the formation of a solution

##### **Molar Heat of Solution**

Enthalpy change associated with the dissolving of one mole of a solute

## **Model for Solids**

### **Types of Solids**

Crystalline Solids - substances in which the particles are arranged in an orderly, geometric, repeating pattern

Amorphous Solids - substances in which the particles are arranged randomly

Definite Shape and Volume

Definite Melting Point

Melting is the physical change of a solid to a liquid by the addition of heat

Melting point is the temperature at which a solid becomes a liquid

- a. Crystalline solids have definite melting points
- b. Amorphous solids do not have definite melting points

### **High Density and Incompressibility**

Low Rate of Diffusion

Two solids in contact will experience VERY SLOW rates of diffusion

### **Crystalline Solids**

Types of crystalline solids (classes of solids)

1. Ionic solids: contains oppositely charged ions

#### Example

Sodium Chloride, NaCl

2. Molecular solids (contains molecules)

#### Examples:

Sucrose

Ice (H<sub>2</sub>O molecules) and Dry ice (CO<sub>2</sub> molecules)

Atomic solid (contains atoms)

#### Examples:

Graphite and diamonds (pure carbon)  
Metals, i.e. Copper

### **Crystal Structure**

The total three-dimensional arrangement of particles of a crystal

### **Unit Cell**

The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice

### **Amorphous Solids**

A. "Amorphous"

1. Greek for "without shape"

B. Formation of amorphous solids

Rapid cooling of molten materials can prevent the formation of crystals

#### Examples:

a. Glass

b. Obsidian (found in lava flows)

### **Bonding in Solids**

1. Ionic solids

Oppositely charged ions packed

High melting points

2. Molecular solids

Fundamental particle is a molecule.

Melt at relatively low temperatures (intermolecular forces are weak)

3. Atomic solids

Variety of properties

# Solutions

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## **Solutions**

1. Types of solutions and factors affecting solubility
2. Methods of expressing concentration (use of normalities is not tested)
3. Raoult's law and colligative properties (nonvolatile solutes); osmosis
4. Nonideal behavior (qualitative aspects)

## **Soluble**

Capable of being dissolved

## **Solution**

A homogeneous mixture of two or more substances in a single phase

## **Solvent**

The dissolving medium in a solution; major component in a solution

## **Solute**

The dissolved substance in a solution

## **Types of solutions**

1. Gaseous mixtures

### Example:

Air is a solution

2. Solid solutions

Metal alloys

### Examples:

(e.g. Brass is a solution of copper and zinc)

3. Liquid solutions

Liquid dissolved in a liquid (alcohol in water)

4. Solid dissolved in a liquid (salt water)

## **Influencing Solvation**

1. Increasing the Surface Area of the Solute (Particle size)

Finely divided substances dissolve more rapidly

## 2. Agitating a Solution

Stirring or shaking brings solvent into contact with more solute particles

Added energy temporarily increases solubility

## 3. Temperature

Heating always increasing the rate of dissolution of solids in liquids

## Solubility

### Solution Equilibrium

The physical state in which the opposing processes of dissolution and crystallization of a solute occur at equal rates

### Saturated solution

A solution that contains the maximum amount of dissolved solute. Additional solute will not dissolve.

### Unsaturated solutions

A solution that contains less solute than a saturated solution under the existing conditions.

### Supersaturated Solutions

A solution that contains more dissolved solute than a saturated solution contains under the same conditions.

### Solubility Values

The solubility of a substance is the amount of that substance required to form a saturated solution with a specific amount of solvent at a specified temperature

The rate at which a substance dissolves does not alter the substances solubility

### Factors Affecting Solubility

#### A. "Like dissolves like"

1. Polar substances dissolve in polar solvents
2. Nonpolar substances dissolve in nonpolar solvents

#### B. Dissolving Ionic Compounds in Aqueous Solutions

1. Electropositive hydrogen of the water molecule is attracted to negatively charged ions
2. Electronegative oxygen of the water molecule is attracted to positively charged ions

### 3. Hydration

The solution process with water as the solvent

### 4. Hydrates

1. Ionic substances that incorporate water molecules into their structure during the recrystallization process  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

a. the "·" means that the water is loosely attached

### C. Nonpolar Solvents

1. Polar and ionic compounds are not soluble in nonpolar solvents

2. Fats, oils and many petroleum products are soluble in nonpolar solvents

3. Nonpolar solvents include  $\text{CCl}_4$  and toluene (methyl benzene),  $\text{C}_6\text{H}_5\text{CH}_3$

### D. Liquid Solutes and Solvents

Immiscible - Liquid solutes and solvents that are not soluble in each other

#### Example:

Oil and water

**Miscible** - Liquids that dissolve freely in one another in any proportion

#### Examples:

Benzene and carbon tetrachloride (both nonpolar)

Water and ethanol (both polar)

### **Effects of Pressure on Solubility**

1. Pressure has no real effect on the solubilities of liquids and solids in liquid solvents

2. Increasing pressure increases the solubility of gases in liquids

### **Effects of Temperature on Solubility**

1. Solubility of solids (generally) increases with temperature

2. Solubility of gases decreases with temperature

### **Units of Concentration**

A solution is described in terms of concentration.

The most common expression of concentration is **molarity** (M)

Molarity is the number of moles of solute per volume of a solution in liters.

$M = \text{molarity} = \text{moles/volume} =$

A one molar solution (1.0 M) contains 1.0 mol of solute per liter of solution.

Note. Sometimes we can rearrange the above equation to solve for the number of moles.

$$M \cdot V = \text{mol}$$

### Sample AP Problem

Determine the mass of KCl (MM = 74.6 g/mol) required to prepare 100 mL of 0.300 M solution.

FOLLOW THE UNITS

$$\frac{0.1 \cancel{\text{ L KCl}}}{1} \times \frac{0.300 \text{ mol KCl}}{1 \cancel{\text{ L KCl}}} \times \frac{74.6 \text{ g KCl}}{1 \text{ mol KCl}} = 2.24 \text{ g KCl}$$

### Molality

Equal to moles of solute per kg of solvent.

**Note.** Molality is used in the freezing point calculations for molar mass.

### Colligative Properties

Physical properties dependent on the type of solute and not the amount of the solute.

Examples:

Vapor pressure, boiling point, freezing point, and osmotic pressure

### Raoult's Law

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^0_{\text{solvent}}$$

in which  $X_{\text{solvent}}$  is the mole fraction

### Boiling Point Elevation

$$\text{Elevation} = \Delta t_{\text{bp}} = k_{\text{bp}} \cdot m_{\text{solute}}$$

in which  $k_{\text{bp}}$  is molal boiling point constant and  $m_{\text{solute}}$  is the molality of solute.

### Freezing Point Depression

$$\text{Depression} = \Delta t_{\text{fp}} = k_{\text{fp}} \cdot m_{\text{solute}} \cdot i$$

in which  $i$  is the **van't Hoff factor**

See Stoichiometry section to see how to calculate molar mass using the freezing point depression.

# Chemical Reactions

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## Reaction types: Overview

1. Acid-base reactions; concepts of Arrhenius, Brønsted-Lowry and Lewis; coordination complexes; amphoterism
2. Precipitation reactions
3. Oxidation-reduction reactions
  - a. Oxidation number
  - b. The role of the electron in oxidation-reduction
  - c. Electrochemistry: electrolytic and galvanic cells; Faraday's laws; standard half-cell potentials; Nernst equation; prediction of the direction of redox reaction

## Reactants

Original substances (reagents) entering into a chemical reaction.

## Products

Products are the resulting substances from a chemical reaction.

Reactants < -- > Products

## Chemical equation

Represents with symbols and formulas, the identities and regular amounts of the reactants and products in a chemical reaction

## Writing Chemical Equations

The equation must represent known facts

This can be done with a word equation:  
"Hydrogen reacts with oxygen to form water"

Hydrogen + Oxygen = Water

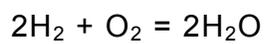
The equation must contain the correct formulas for reactants and products

This is done with a formula equation

$\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$

The law of conservation of atoms must be satisfied

Balancing is done with coefficients-small whole numbers that appear in fronts of a formula



+ Used to separate two reactants or products

double arrow "Yields," separates reactants from products

1 Used in place of a single arrow to indicate reversible reactions

(s) Reactant or product in the solid state. Also a precipitate

(l) Reactant or product in the liquid state.

(aq) Reactant or product in an aqueous solution (dissolved in water)

(g) Reactant or product in the gaseous state

$\Delta$  or heat Reactants are heated

Pt A formula written above or below the yield sign indicates its use as a catalyst (in this case, platinum)

Pressure Pressure at which reaction is carried out exceeds normal atmospheric pressure

25 °C Temperature at which the reaction is carried out, in this case 25 °C

# Acid-Base Chemistry

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## Acid-base reactions

Concepts of Arrhenius, Brønsted-Lowry and Lewis; coordination complexes; amphoterism

### General Properties of acids and bases

1. Properties of acids:
  - a) React with metals to give hydrogen.
  - b) Neutralize bases.
  - c) Taste sour.
  - d) Change blue litmus paper to red.

2. Properties of bases:
  - a) Emulsify fats and oils.
  - b) Neutralize acids.
  - c) Taste bitter.
  - d) Change red litmus paper to blue.

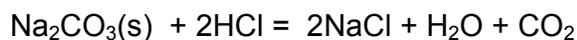
Lichens produce a dye called litmus. Lichens are also known as brown alga, a symbiotic relationship between a fungi and alga organisms.

**Note:** Many indicators exist.

### Properties of Acids (revisited)

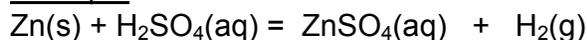
1. Aqueous solutions have a sour taste
2. Acids change the color of acid-base indicators
3. Acids react with carbonates to produce water, a salt, and carbon dioxide

Example:



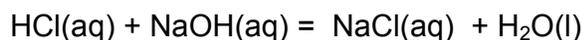
4. Some acids react with active metals to release hydrogen

Example:



5. Acids react with bases to produce salts and water (neutralization)

Example:



6. Acids conduct electric current (electrolytes)
7. Acids donate a proton ( $\text{H}^+$ )
8. Acids have a pH below 7

**Properties of Bases (revisited)**

1. Aqueous solutions of bases have a bitter taste
2. Bases change the color of acid-base indicators
3. Dilute aqueous solutions of bases feel slippery
4. Bases react with acids to produce salts and water
5. Bases conduct electric current

**The Arrhenius definition**

1. An Arrhenius acid is any chemical substance that dissociates in water with release of  $\text{H}^+$  ions.

**Note:** A hydronium ion ( $\text{H}_3\text{O}^+$ ) is one way to designate a hydrogen ion because the hydrogen ion does not exist alone but is surrounded by water.

2. An Arrhenius base is any chemical substance that dissociates in water with liberation of  $\text{OH}^-$  ions (hydroxide ions).

3. The Arrhenius definition is used in writing the chemical formula of most common acids and bases.

a) An Acid is any electrolytic compound whose chemical formula begins in "H" for the hydrogen ion ( $\text{H}^+$ ).

An **electrolytic compound** is any substance freely giving off ions.

b) The subscript of the hydrogen in an acid formula gives the number of hydrogen ions that dissociate in solution.

(1) Acids with only one hydrogen ion in their formulas are said to be monoprotic. Hydrochloric acid,  $\text{HCl}$  is a monoprotic acid.

(2) Acids with two hydrogen ions in their formulas are said to be diprotic. Sulfuric acid,  $\text{H}_2\text{SO}_4$  is a diprotic acid.

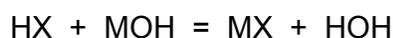
(3) And acids with three hydrogen ions in their formulas are said to be triprotic. Phosphoric acid,  $\text{H}_3\text{PO}_4$  is a triprotic acid.

c) A base is any electrolytic compound whose chemical formula ends in "OH" for the hydroxide ion ( $\text{OH}^-$ ).

4. The Arrhenius definition also includes the terms neutralization and salt.

a) **Neutralization** in this sense means the result of mixing an acid with a base and obtaining a neutral solution.

(1) The characteristic equation representing neutralization is:

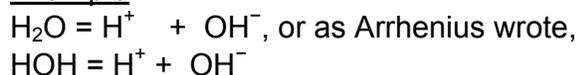


Where HX represents the Arrhenius acid, MOH represents the Arrhenius base, MX is the salt formed in the neutralization, and HOH is the Arrhenius representation of water.

(2) Notice the Arrhenius representation of water from above. Arrhenius was once asked whether water is an acid, a base, both, or neither. His answer was, "Yes."

(a) Water self-ionizes to form hydrogen ion and hydroxide ion:

Example:



### The Brønsted-Lowry definition

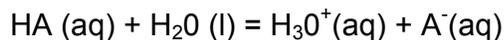
1. Arrhenius concept of acids and bases only includes the hydroxide ion.

2. Brønsted and Lowry independently defined acids and bases by a proton.

3. An acid is a proton ( $\text{H}^+$ ) donor. An acid is designated HA.

4. A base is a proton ( $\text{H}^+$ ) acceptor.

5. The representation of a general acid-base reaction.



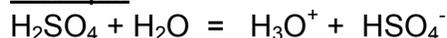
**Note: Compare this representation to Arrhenius.**

HA represents the acid;  $\text{A}^-$  represents the base.

H<sub>2</sub>O is a base (conjugate base), H<sub>3</sub>O<sup>+</sup> is an acid (conjugate acid)

6. Conjugate acid-base pair consists of a single proton accepted or donated by two substances.

Example:



H<sub>2</sub>SO<sub>4</sub> is the acid – which is the conjugate base? (Answer: HSO<sub>4</sub><sup>-</sup>)

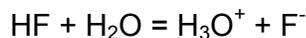
### Sample AP Question

Which of the following represents conjugate acid-base pairs?

- a. HF, F<sup>-</sup>
- b. NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>
- c. HCl, H<sub>2</sub>O
- d. HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>CO<sub>3</sub>

Look for the difference between a proton in which an acid donates a proton (H<sup>+</sup>).

Consider the following equation:



### Lewis Acids-Bases

Lewis Acid accepts a pair of electrons

Lewis Base donates a pair of electrons

### Acid strength

1. The strength of an acid is determined by how much H<sup>+</sup> it liberates in water solutions. The more H<sup>+</sup>, the stronger the acid.
2. [H<sup>+</sup>], which is read “hydrogen ion concentration,” is the molarity of the H<sup>+</sup>. The higher this molarity is, the stronger the acid.

### Base strength

1. The strength of a base is determined by how much OH<sup>-</sup> it liberates in water solutions. The more OH<sup>-</sup>, the stronger the base.
2. [OH<sup>-</sup>], which is read “hydroxide ion concentration,” is the molarity of the OH<sup>-</sup>. The higher this molarity is, the stronger the base.

## pH scale (pH = 1 - 14)

1. The pH scale is used to compare the strength of acids and bases.
2.  $\text{pH} = -\log [\text{H}^+]$  “the negative log of the hydrogen ion concentration”
3. For water,  $\text{pH} = -\log(1.00 \times 10^{-7}) = 7$ .
4. For acids,  $\text{pH} < 7$  since acid solutions have  $[\text{H}^+] > 1.00 \times 10^{-7} \text{ M}$ .
5. Any  $\text{pH} > 7$  corresponds to a base.

## pOH and bases

1. Shouldn't pOH be used to compare the strength of bases?
2.  $\text{pOH} = -\log [\text{OH}^-]$
3. For neutral solution,  
 $\text{pOH} = -\log(1.00 \times 10^{-7}) = 7$ , exactly the same value as pH.
4.  $\text{pH} + \text{pOH} = 14$ . This means that for any pOH there is a corresponding pH, and allows us to use just the pH scale for both acids and bases.

## Calculating pH

### Sample problems

What is the pH of a base with a pOH value of 3?

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + 3 = 14$$

$$\text{pH} = 11$$

What pH corresponds to  $[\text{H}^+] = 2.13 \times 10^{-5}$ ?

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log (2.13 \times 10^{-5})$$

$$\text{pH} = 4.672$$

Calculate the molarity of a solution with a pH = 1.23.

$$\text{pH} = -\log [\text{H}^+]$$

$$1.23 = -\log [\text{H}^+]$$

$$-1.23 = \log [\text{H}^+]$$

$$\text{antilog} (-1.23) = [\text{H}^+]$$

$$5.8 \times 10^{-2} = [\text{H}^+]$$

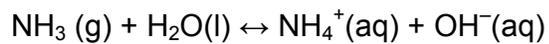
### **Amphoteric Substances**

Substances that can act as an acid in one reaction and as a base in another are called amphoteric substances.

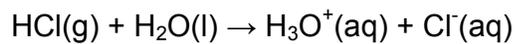
#### Example:

Water can donate or accept protons.

Water donates proton (acid)



Water accepts proton (base)



# Precipitation

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## Precipitation reactions

Precipitate reactions are exchange reactions driven forward by the formation of an insoluble salt known as a precipitate.

Reactions may be written three ways:

1. Molecular formulas using (aq), (g), (s), and (l)
2. Reactions showing the ions involved in the reaction; showing only the molecular formula of the solid.
3. Net ionic equation, without spectator ions shown in the equation.

### Precipitate

A solid that forms during a chemical reaction. Look for the (s) next to the molecular formula in a chemical equation.

### Insoluble

Does not stay in solution, cannot be dissolved.

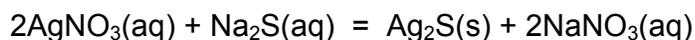
### Soluble

Stays in solution, dissolves. Look for the (aq) next to the formula in a chemical equation.

### Spectator ions

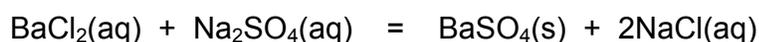
Ions not involved in a chemical reaction.

### Example #1



This is an **exchange reaction** in which the metals exchange anions. Rule number 4 below states most silver salts are insoluble.

### Example #2



This is an **exchange reaction** in which the barium exchanges chloride with sulfate. The reaction is driven forward by the precipitate.

Sulfates are exceptions to rule #5.

**Memorize the solubility rules - today!**

### **Solubility Rules**

1. Salts containing Group I elements are soluble ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ). Exceptions to this rule are rare. Salts containing the ammonium ion ( $\text{NH}_4^+$ ) are also soluble.

2. Salts containing nitrate ion ( $\text{NO}_3^-$ ) are generally soluble.

3. Salts containing halogens such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  are generally soluble. Important exceptions to this rule are halide salts of  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ , and  $(\text{Hg}_2)^{2+}$ . Thus,  $\text{AgCl}$ ,  $\text{PbBr}_2$ , and  $\text{Hg}_2\text{Cl}_2$  are all insoluble.

4. Most silver salts are insoluble.  $\text{AgNO}_3$  and  $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$  are common soluble salts of silver; virtually anything else is insoluble.

5. Most sulfate salts are soluble. Important exceptions to this rule include  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{Ag}_2\text{SO}_4$  and  $\text{SrSO}_4$ .

6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and  $\text{Al}^{3+}$  are insoluble. Thus,  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Co}(\text{OH})_2$  are not soluble.

7. Most sulfides of transition metals are highly insoluble. Thus,  $\text{CdS}$ ,  $\text{FeS}$ ,  $\text{ZnS}$ ,  $\text{Ag}_2\text{S}$  are all insoluble. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.

8. Carbonates are frequently insoluble. Group II carbonates (Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include  $\text{FeCO}_3$  and  $\text{PbCO}_3$ .

9. Chromates are frequently insoluble.

Examples:

$\text{PbCrO}_4$ ,  $\text{BaCrO}_4$

10. Phosphates are frequently insoluble.

Examples:

$\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Ag}_3\text{PO}_4$

11. Fluorides are frequently insoluble.

Examples:

BaF<sub>2</sub>, MgF<sub>2</sub>, PbF<sub>2</sub>.

**Memorize the following information:**

NH <sub>4</sub> NO <sub>3</sub>	soluble
NH <sub>4</sub> Br	soluble
Ag <sub>2</sub> O	insoluble
AgBr	insoluble
Pb(NO <sub>3</sub> ) <sub>2</sub>	soluble
Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	insoluble
MgS	insoluble
Na <sub>3</sub> PO <sub>4</sub>	soluble
Ca(OH) <sub>2</sub>	insoluble
CaCO <sub>3</sub>	insoluble
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	soluble
CaSO <sub>4</sub>	soluble
Ag <sub>2</sub> SO <sub>4</sub>	soluble
PbCl <sub>2</sub>	insoluble
SrSO <sub>4</sub>	insoluble
Fe(OH) <sub>3</sub>	insoluble
Co(ClO <sub>4</sub> ) <sub>2</sub>	soluble
Ba(ClO <sub>3</sub> ) <sub>2</sub>	soluble
CaS	insoluble
BaSO <sub>4</sub>	insoluble
LiC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	soluble
PbO	insoluble
SnCO <sub>3</sub>	insoluble
MgI <sub>2</sub>	soluble
BaBr <sub>2</sub>	soluble
Ba(OH) <sub>2</sub>	insoluble
CsOH	soluble
BaSO <sub>3</sub>	insoluble
Na <sub>2</sub> SO <sub>3</sub>	soluble
K <sub>2</sub> O	soluble
Mg(NO <sub>3</sub> ) <sub>2</sub>	soluble
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	insoluble
FeSO <sub>4</sub>	soluble
Ga <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	soluble
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	soluble

Be(OH) <sub>2</sub>	soluble
Mg(OH) <sub>2</sub>	insoluble
FeS	insoluble
(NH <sub>4</sub> ) <sub>2</sub> O	soluble
AgClO <sub>3</sub>	soluble
Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	soluble
Fe(ClO <sub>4</sub> ) <sub>2</sub>	soluble
MgSO <sub>4</sub>	soluble
AgCl	insoluble
AlBr <sub>3</sub>	soluble
FeBr <sub>3</sub>	soluble
Ca(NO <sub>3</sub> ) <sub>2</sub>	soluble
MgCO <sub>3</sub>	insoluble
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	soluble
Li <sub>2</sub> CO <sub>3</sub>	soluble
K <sub>2</sub> SO <sub>4</sub>	soluble
K <sub>3</sub> PO <sub>4</sub>	soluble
SnS	insoluble
Al <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	insoluble
Mn(OH) <sub>3</sub>	insoluble

# Electrochemistry

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## Oxidation-reduction reactions

- Oxidation number
- The role of the electron in oxidation-reduction
- Electrochemistry: electrolytic and galvanic cells; Faraday's laws; standard half-cell potentials; Nernst equation; prediction of the direction of redox reaction

## Oxidation number

The charge that an atom would have if electrons were transferred or gained.

Useful for predicting the formula of an ionic compound.

## Rules for Determining Oxidation Number

Use the group number in the periodic table to help you. Learn the exceptions.

1. Free elements that have not lost or gained electrons, each atom has an oxidation number of zero.

Example:

$\text{N}_2$ , the oxidation number of each nitrogen atom is zero.

2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion.

Example:

$\text{Ca}^{2+}$  is +2,  $\text{K}^+$  is +1.

3. All alkali metals (elements in column 1 of the periodic table, with the exception of hydrogen) have an oxidation number of +1.

Example:

Li, K, and Na will always be +1.

4. All alkaline earth metals (elements in column 2 of the periodic table) have an oxidation number of +2.

Example:

Mg, Ba, and Ca is +2.

5. The oxidation number of Aluminum (Al) is always +3.

6. The oxidation number of oxygen in most compounds is -2.

Example (oxidation of -2)

such as H<sub>2</sub>O and CO<sub>2</sub>

Example (exception)

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and peroxide (O<sub>2</sub><sup>2-</sup>) oxygen shows a -1 oxidation number.

7. The oxidation number of hydrogen is +1, except when it is bonded to a metal as a negative ion, in which case it is -1.

Example:

H<sub>2</sub>O shows hydrogen as +1. NaH shows hydrogen as -1.

8. When halogens (elements in column 17 on the periodic table) form negative ions, they will have an oxidation number of -1.

Example:

NaCl and CaCl<sub>2</sub> both show chlorine with a -1 oxidation number.

Exceptions:

Chlorine combined with nonmetals

9. In a neutral molecule, the sum of the oxidation numbers of all of the atoms must be zero.

Example:

In H<sub>2</sub>O, each hydrogen is +1 and the oxygen is -2. So, (2 x +1) + (-2) = 0.

10. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

Example:

In the polyatomic ion known as hydroxide (OH<sup>-</sup>), the oxygen is -2 and the hydrogen is +1. So, (-2) + (+1) = -1, the same as the charge on the hydroxide ion (OH<sup>-</sup>)

11. Some metals show different positive oxidation numbers, in different situations. Use Alfred Stock's system; use parenthesis to identify the number of electrons lost by the metal.

Example:

Copper(I) and Copper(II), Iron(II) and Iron(III)

### **Sample AP Problem**

What is the oxidation state of chromium in the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$ ?

Oxygen adds to  $-14 = (7 \times -2)$ , Two Cr ions add to 12 plus 2 electrons spread throughout the polyatomic. Divide 12 by 2 and get oxidation number of 6.

## Electrochemistry

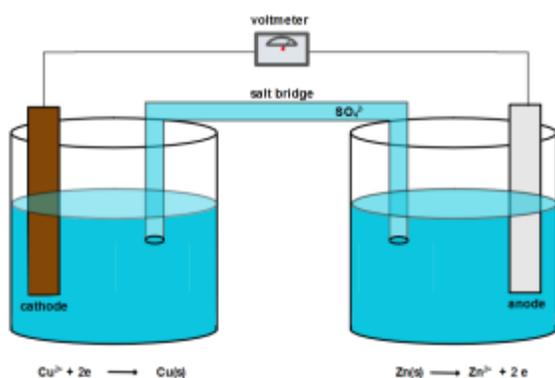
The study of redox reactions; the transfer of charges

### Electrolytic and galvanic cells

An apparatus used to drive the flow of electrons

Example:

250 mL of 1.0 M  $\text{CuSO}_4$  and 250 mL of 1.0 M  $\text{ZnSO}_4$



$\text{Zn(s)} = \text{Zn}^{2+} + 2\text{e}^-$  (anode, oxidation)

$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu(s)}$  (cathode, reduction)

-----  
 $\text{Zn(s)} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu(s)}$

The **anode** is the place of **oxidation**, the loss of electrons. The **cathode** is the place of **reduction**, the gain of electron (the charge is reduced).

### Shorthand

$\text{Zn(s)} \mid \text{Zn}^{2+} (1.0\text{M}) \parallel \text{Cu}^{2+}(1.0\text{M}) \mid \text{Cu(s)}$

oxidation || reduction

### Standard half-cell potentials

### Faraday's laws

First Law of Electrolysis

"The amount of any substance deposited, evolved, or dissolved at an electrode is directly proportional to the amount of electrical charge passing through the circuit."

$Q = It$ , where  $Q$  is charge,  $I$  is current, and  $t$  is time

A charge of an electron:  $1.602 \times 10^{-19}$  C

Avogadro's number:  $6.022 \times 10^{23}$

To get the charge of one mole of electrons, multiply the charge of one electron by Avogadro's number. This is known as **Faraday's constant** ( $F$ ) =  $9.65 \times 10^4$

### Second Law of Electrolysis

"The mass of different substances produced by the same quantity of electricity are directly proportional to the molar masses of the substances concerned, and inversely proportional to the number of electrons in the relevant half-reaction."

This means two moles of electrons are lost by zinc in our example.

### **Nernst equation**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

**Note.** The Nernst equation is plug-n-chug.

### **Predictions**

Use the standards potential table provided during the AP Chemistry exam to determine whether a reaction moves in one direction or another.

In our Zinc || Copper example, The  $E_0$  for zinc is greater than copper; therefore, the zinc's potential for undergoing oxidation is greater.

# Stoichiometry

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## Stoichiometry

1. Ionic and molecular species present in chemical systems: net ionic equations
2. Balancing of equations, including those for redox reactions
3. Mass and volume relations with emphasis on the mole concept, including empirical formulas and limiting reactant

### Balancing equations

Balanced equations follow the law of conservation of matter; that is, we do not create nor destroy atoms but simply rearrange them during a chemical reaction.

Simple equations may be balanced through inspection. Simply change coefficients of the molecules (not the subscripts) until all atoms on both sides of the arrow are equal.

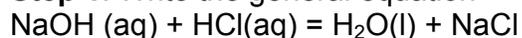
**Balancing net ionic equations** is a little more complex but can be completed in three steps.

1. Write the general equation
2. Write the total ionic equation
3. Write the net ionic equation (remove spectator ions)

### Sample Problem

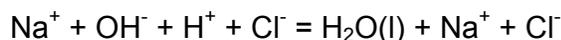
Write the balanced net ionic equation for the reaction of aqueous sodium hydroxide and aqueous hydrochloric acid

**Step 1:** Write the general equation



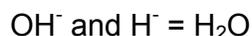
The equation is balanced: The number of atoms on the left and right are the same.

**Step 2:** Write the total ionic equation



**Step 3:** Write the net ionic equation (remove spectators)

$\text{Na}^+$  and  $\text{Cl}^-$  did not undergo reduction or oxidation. They are removed, leaving:



### Mole

The SI Unit mole is a quantity. Just as we say "a dozen donuts" when we mean 12 donuts, chemists say "a mole of substance" to mean  $6.02 \times 10^{23}$ . The mole is a number.

### Molar mass

Two concepts are important. First, molar mass of a molecule is the sum of all masses of the atoms in the molecule. Second, values for each element are found on the periodic table. Simply take the "A" number, the average atomic mass, and this is equal to the number of grams per mole.

### **Empirical formulas**

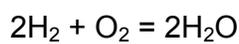
The simplest formula showing all of the atoms in a molecule.

### **Limiting reactants (reagents)**

If you decided to make two hamburgers, but only had one meat patty, then you are limited to only one hamburger, right? The same principle is applied to chemical reactions.

#### Example:

Consider the following reaction:



What happens if we are provided with all of the oxygen needed (excess oxygen) but only given 1 mole of hydrogen gas?

The hydrogen limits the reaction so that only 1 mole of water is produced. This is because the ratio of hydrogen gas to the water produced is 1 to 1.

What happens if we are provided with all of the hydrogen needed (excess hydrogen) but only given 1 mole of oxygen gas?

The oxygen limits the reaction so that 2 moles of water are produced. This is because the ratio of oxygen gas to water produced is 1 to 2.

# Equilibrium

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## Equilibrium

1. Concept of dynamic equilibrium, physical and chemical; Le Chatelier's principle; equilibrium constants
2. Quantitative treatment
  - a. Equilibrium constants for gaseous reactions:  $K_p$ ,  $K_c$
  - b. Equilibrium constants for reactions in solution
    - (1) Constants for acids and bases;  $pK$ ;  $pH$
    - (2) Solubility product constants and their application to precipitation and the dissolution of slightly soluble compounds
    - (3) Common ion effect; buffers; hydrolysis

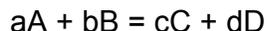
## The Equilibrium Condition

Equilibrium is not static, but is a highly dynamic state. At the macro level everything appears to have stopped but at the molecular level, there is frantic activity. The concentration of products builds as the reaction proceeds. There will come a time, in some reactions, where the products will collide and thus react and reform the reactants. When both the forward and reverse reaction occur at the same rate there is no change in concentration reactants and products and the reaction is said to be at equilibrium.

A double arrow (or  $\rightleftharpoons$ ) is used to show that a reaction can occur in either direction.

## The Equilibrium Constant

Let us use the following equation:



where A, B, C, and D represent chemical species and a, b, c, and d are their coefficients in the balanced equation.

Since the concentration of the products and reactants remains constant at equilibrium, we can set up a mass action expression: Which is the concentration of the products (raised to the power of their coefficients) divided by the concentration of the reactants (raised to the power of their coefficients).

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This mass action expression can then be used to find a constant for the reaction at a given temperature. This constant is known as the equilibrium expression ( $K_c$  or  $K_{eq}$ ). To change this into an equilibrium expression, set it equal to  $K_c$ .

### Three conclusions about the equilibrium expression:

1. The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
2. When the balanced equation for a reaction is multiplied by a factor  $n$ , the equilibrium expression for the new reaction is the original expression raised to the  $n$ th power. Thus  $K_{new} = (K_{original})^n$ .
3. The units for  $K$  are determined by the powers of the various concentration terms. The units for  $K$  therefore depend on the reaction being considered.

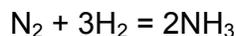
**Equilibrium position** - set of equilibrium concentrations. There is only one equilibrium constant for a particular system at a particular temperature, but there are an infinite number of equilibrium positions. This can tell us in what direction the reaction will proceed.

### Equilibrium Expressions Involving Pressures

How is pressure related to concentration?

A couple of chapters ago we rearranged the ideal gas law to include molarity (except this time we are going to use  $C$  for concentration) - Where  $C$  equals  $n/V$ , or the number of moles  $n$  of gas per unit volume  $V$ . Thus  $C$  represents the molar concentration of the gas.

If we examine this in terms of the Haber process:



we see that the equilibrium expression would look like - or in terms of the equilibrium partial pressures of the gases -

Since we learned there is a relationship which exists between concentration and pressure, so there must be a relationship between  $K$  and  $K_p$

$$K_p = K(RT)^{\Delta n}$$

where " $\Delta n$ " is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

## Homogeneous and Heterogeneous Equilibria

### Homogeneous equilibria

All reactants and products are all the same phase (e.g., all gaseous).

### Heterogeneous equilibria

All reactants and products are not in the same phase. These equilibria do not depend on the amounts of pure solids or liquids present (i.e. pure solids and liquids are not included in the equilibrium expression).

## Factors Affecting Equilibrium: Le Châtelier's Principle

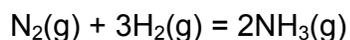
### A. Le Châtelier's Principle

1. When a closed system at equilibrium is disturbed by application of a stress, it attains a new equilibrium position that minimizes the stress

### B. Equilibrium and System Stresses – Predicting the direction of shift

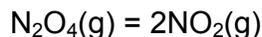
#### 1. Pressure

a. An increase in pressure will cause the reaction to shift in the direction that result in fewer collisions – toward the side of the reaction with the least number of moles of gas molecules



An increase in pressure causes the equilibrium position to shift to the right, where there are only two moles of gas. The left side has four moles of gas

b. Decreases in pressure cause the reaction to shift in the direction that increases collisions; toward the side with more moles of gas



A decrease in pressure causes the equilibrium position to shift to the right, because there are more moles of gas (2 moles) than on the left (1 mole)

c. Pressure has no effect on equilibrium if there are no gas phase reactants or products

#### 2. Temperature

a. Increasing temperature causes the reaction to shift in a way so as to use up the added energy (away from the side that has energy)

Endothermic reaction



Exothermic reaction



b. Decreasing temperature causes the reaction to shift in a way so as to replace the missing energy (toward the side that has energy)

### 3. Concentration

a. Increasing the concentration of a reactant or product causes the reaction to shift in such a way as to try to use up the added substance (away from that substance)

Increasing [X] or [Y]



The reaction shifts away from [X] and [Y] and produces more [Z]

b. Decreasing the concentration of a reactant or product causes the reaction to shift in such a way as to try to replace the missing substance (toward that substance)

Result of decreasing [X] or [Y]



The reaction shifts toward [X] and [Y] and produces more [X] and [Y]

# Kinetics

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## **Kinetics**

1. Concept of rate of reaction
2. Use of experimental data and graphical analysis to determine reactant order, rate constants and reaction rate laws
3. Effect of temperature change on rates
4. Energy of activation; the role of catalysts
5. The relationship between the rate-determining step and a mechanism

## **Collision Theory**

- A. The Collision theory explains characteristics of chemical reactions.
1. Higher concentrations lead to faster reaction rates.
  2. Higher temperatures lead to greater energy to break bonds
- B. Particles must collide while favorably oriented
- C. Particles must collide with enough energy to disrupt the bonds of the molecules
- D. Reaction rate
1. The rate of disappearance of reactants
  2. The rate of appearance of products
- E. Activated Complex
1. A transitional structure resulting from an effective collision that persists while old bonds are breaking and new bonds are forming
- F. Activation Energy ( $E_a$ )
1. The minimum energy required to transform reactants into the activated complex
- G. Sources of Activation Energy
1. Flame, spark, high temperature, radiation

## **Conditions that Affect Reaction Rates**

- A. Nature of the Reactants
1. Rate depends on the particular bonds involved
- B. Amount of Surface (particle size)
1. The more surface area of a solid exposed, the faster the rxn

### C. Temperature

1. Rates of reactions are roughly doubled for every 10 °C increase in temperature

- a. increase in collision energy
- b. increase in collision frequency

### D. Effect of Concentration

1. Increasing concentrations of liquid or gaseous solutions usually increases rates of reaction

2. Actual effect of concentration change must be determined experimentally for each reaction

### E. Presence of Catalysts

1. A catalyst is a substance of substances that increase the rate of a chemical rxn without itself being changed

2. Catalysts provide an alternate reaction mechanism or pathway with a lower activation energy

### Catalysts in Detail

A catalyst is a substance which alters the rate of a chemical reaction but is chemical unchanged at the end of the chemical reaction.

1. The phrase catalyzed processes was coined by Jöns Jakob Berzelius in 1836

2. Only small quantities are required.

a. Catalysts are not changed during a chemical reaction.

3. Alter the rate of a reaction

a. Speed up a reaction

i. "Positive catalysts" or "promoters"

ii. "Negative catalysts" or "inhibitors"

4. Do not alter the position of equilibrium

5. Enzymes are biological catalysts

a. Enzymes are catalysts in metabolism and catabolism.

b. Enzymes are very specific

6. Using the Kinetic Molecular Theory, catalysts increase the chance molecules collide.

a. Intermediate compounds arrange the surface of the substances to collide in the proper orientation.

- b. Transition state theory. Products and reactants are in equilibrium with an intermediate “activated complex” or “transition state.”
- c. Activation energy ( $E_a$ ) is lowered because a “different path” to the reaction occurs; that is, the transition state (activated complex) requires lower activation energy.

## Reaction Orders

Reaction orders are determined experimentally.

### Rate Law

The instantaneous rate (the slope of the curve) as a function of concentration.

$$\text{rate} = k[A]^a [B]^b [C]^c$$

Chemists determine the order of the reaction by adding the exponents.

### Zero Order Reactions

Reaction rates that are **independent** of the concentrations of the reactions have a rate law shown:

$$\text{rate} = k, \text{ with the units M/sec}$$

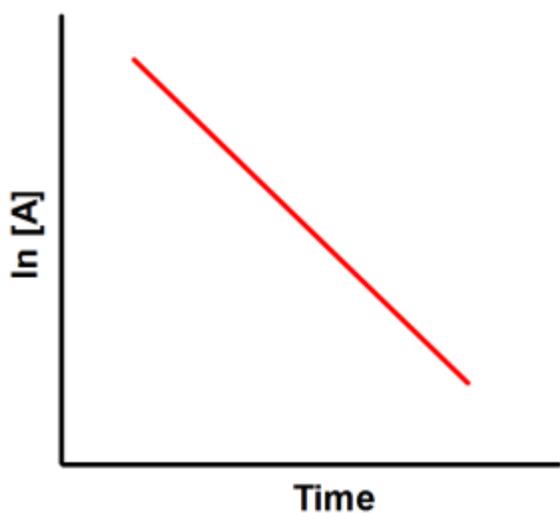
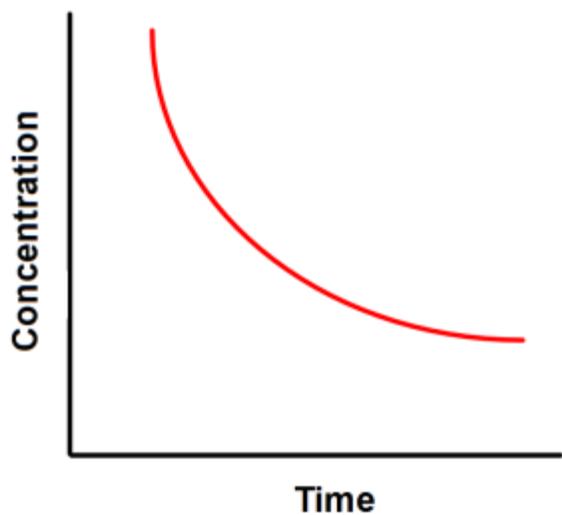
### First Order

Reactions with rates **proportional** to one of the reactants is shown:

$$\text{rate} = k [A], \text{ with units of sec}^{-1}$$

Doubling the concentration increases the rate by a factor of 2.

## Graphs of First Order



**Note:** Half-life is a first order reaction.

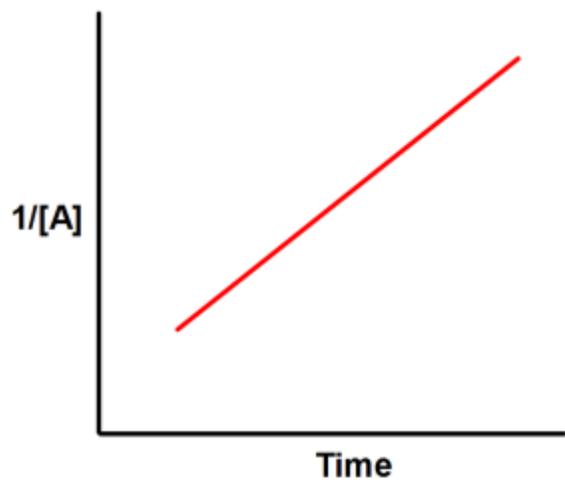
### **Second Order**

The rate is proportional to the concentration of the square of a single reactant OR the product of the concentration of two reactants.

$$\text{rate} = k[A]^2$$

Doubling the concentration increases the rate by a factor of 4.

### **Graphs of Second Order**



# Thermodynamics

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## Thermodynamics

1. State functions
2. First law: change in enthalpy; heat of formation; heat of reaction; Hess's law; heats of vaporization and fusion; calorimetry
3. Second law: entropy; free energy of formation; free energy of reaction; dependence of change in free energy on enthalpy and entropy changes
4. Relationship of change in free energy to equilibrium constants and electrode potential

## Temperature

1. A measure of the average kinetic energy of the particles in a sample of matter
2. A measure of the random motion of the components of a substance.

## Heat (or Heat Energy)

1. Heat is a flow of energy due to a temperature difference.
2. The sum total of the kinetic energies of the particles in a sample of matter
  - a. Heat flows spontaneously from matter at higher temperature to matter at lower temperature

## Energy

1. The ability to work or produce heat
  - a. Potential energy
    - i. energy due to position or composition
  - b. Kinetic energy
    - i. energy due to an object's motion
    - ii.  $KE = \frac{1}{2} mv^2$

## Law of conservation of energy

- a. A law is a summary of observations
- b. energy can be converted from one form to another but cannot be neither created nor destroyed
- c. Energy of the universe is constant

## State function

Property independent of its path

## Examples:

Enthalpy, entropy, and free energy

## First Law of Thermodynamics

Energy cannot be created or destroyed, but only changed from one form to another.

### Specific Heat

The amount of heat required to raise the temperature of one gram of substance by one Celsius degree ( $1^{\circ}\text{C}$ ) or one Kelvin ( $1\text{ K}$ )

Metals have a very low specific heat. In contrast, water has a high specific heat.

$$C_p = q / m \times T$$

### Sample AP Problem

A metal has a mass of 20.0 g is heated to  $70^{\circ}\text{C}$  and placed in 100 g of water with an initial temperature of  $20^{\circ}\text{C}$ . The water temperature increases to  $23^{\circ}\text{C}$ . Find the specific heat of the metal.

This is solved in two steps. First, find the  $q$  of the water. Next, assume the  $q$  of the water and metal are the same (energy is transferred and not lost).

$$\begin{aligned} q_{\text{water}} &= \text{mass} (C_p) \Delta T \\ &= 100\text{ g} \times (4.184\text{ J / g }^{\circ}\text{C}) \times (23 - 20^{\circ}\text{C}) \\ &= 1255\text{ Joules} \end{aligned}$$

Now use this value with the information for the metal

$$\begin{aligned} 1255\text{ J} &= 20.0\text{ g} (C_p)(70 - 23^{\circ}\text{C}) \\ 1255\text{ J} &= 940 (C_p) \\ 1.34\text{ J / g }^{\circ}\text{C} &= (C_p) \end{aligned}$$

### Enthalpy Change ( $\Delta H$ )

1. The amount of heat absorbed or lost by a system during a process at constant temperature

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

### Endothermic and Exothermic

$\Delta H$  is positive for an endothermic reaction

(1) Heat content of products is greater than the heat content of the reactants

$\Delta H$  is negative for an exothermic reaction

(1) Heat content of the reactants is greater than the heat content of the products

#### A. Writing Thermochemical Equations

1. Fraction coefficients may be used because coefficients represent mole quantities, not atoms or molecules
2. Use appropriate state/phase symbols  
(g) (l) (s)
3.  $\Delta H$  is proportional to the number of moles
4.  $\Delta H$  is usually not influenced significantly by the temperature of the system

#### Hess's Law

The overall enthalpy of a reaction is the sum of all the reactions for the process.

#### Second Law of Thermodynamics

Entropy or disorder of the universe will increase over time

Entropy is a measure of disorder

1. Entropies of phases gases > liquids > solids
2. Entropies are greater for larger molecules

If  $\Delta S$  is negative then fewer products are formed

If  $\Delta S$  is positive then more products are formed

#### Gibbs Free Energy

The amount of energy in a reaction that can be used for work

#### Relationship of change in free energy to equilibrium constants and electrode potential

$$\Delta G^0 = -RT \ln K$$

R = Universal gas law constant

T = Temperature (Kelvin)

K = Equilibrium constant

# Laboratory

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## **Lab 1 Determine the formula of a compound**

Silver oxide is placed in a crucible. A bunsen burner is used to burn off oxygen. Silver remains in the crucible. Students keep track of the masses, calculate moles, determine the mole ratio which is the subscripts of an empirical formula.

## **Lab 2 Determination of the percentage of water in a hydrate**

Students place alum in a crucible and heat using a bunsen burner. The anhydrate  $\text{AlK}(\text{SO}_4)$  remains. Students keep track of the masses, calculate moles, determine mole ratio.

## **Lab 3 Determination of the Molar Mass of volatile liquids**

Volatile liquid is placed in a pipet and allowed to vaporize after placing in boiling water. The pipet cools and the liquid vapor condenses. Volume is calculated using the density of water and water mass placed in the Ideal Gas Law Equation.

Lab 4 Molar Mass by Freezing Point Depression

Lab 5 Determination Molar Volume of a Gas

Lab 6 Acid-Base Titration

Lab 7 Acid-Base Titration

Lab 8 Determination of Concentration by Redox

Lab 9 Determination of Mass and Mole Relationships in a Chemical Reaction

Lab 10 Determination of the Equilibrium Constant for a Chemical Reaction of Weak Acids

Lab 11 Indicators

Lab 12 Determination of the Rate of the Reaction and its Order

Lab 13 Determination of the Enthalpy Change

Lab 14 Cations and Anions

Lab 15 Coordination Compounds

Lab 16 Analytical Gravimetric Analysis

Lab 17

## **Lab 18: Chromatography**

Dyes are placed on chromatography paper and placed in a solvent. The dyes move and separate.

$R_f = \text{component distance} / \text{solvent distance}$

Based on the sample results below, which dyes are in the unknown?

<<IMAGE1>>

The unknown is a mixture of dyes 1 and 2.

Lab 19

Lab 20 Electrochemical Series

Lab 21

Lab 22 Organic Compounds